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Rusty Blanski (PRSM); Justin Leland (ERC); Brent Viers (PRSM); Shawn Phillips (PRSM), "High Temperature Lubricants Based on Polyhedral Oligomeric Silsesquioxanes (POSS)"

SAMPE Spring Meeting (General Audience) **(Statement A)**
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HIGH TEMPERATURE LUBRICANTS BASED ON POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS)

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ABSTRACT

Lubricants that operate at high temperature can be useful for high performance jet turbines. The challenges that have to be overcome for high performance turbines are two fold. The first challenge is increasing the operating temperature of the system while the second challenge is maintaining low temperature pumpability. We have been investigating the use of POSS compounds for lubrication applications because of its proven high temperature stability and its access to a diverse array of silsesquioxane geometries that may be amenable to low temperature pumpability. Consequently, a wide array of POSS alkyls were synthesized and tested for temperature stability and viscosity profiles. The synthesis of these POSS alkyls as well as the relevant temperature and viscosity data will be discussed.

KEY WORDS: Lubrication, POSS, silsesquioxane, turbine, high temperature

1. INTRODUCTION

Current polyester technology for turbine jet engine lubricants has an upper use temperature limit of 400°F with almost no alternatives available for significant temperature increases. As operating temperatures in gas turbine engines increase, engine manufacturers need a lubricant that can operate between -40°F and at least 450°F. We have developed a polyhedral oligomeric silsesquioxane (POSS)-based lubricant that meets the low-temperature end of the performance range and approaches the high-temperature minimum for a functional lubricant.

A current Air Force base stock, the main component of current aircraft lubrication systems, is a mixture of trimethylopropane and pentaerithritol fatty acid esters. Since each of these molecules has a relatively low molecular weight (~450-600 g/mole), previous researchers developed the pentaerithritol dimer hexaester $(R_3OCH_2)_3CCH_2OCH_2C(CH_2OR)_3$ (Figure 1) (1). Along these lines, we searched for a higher molecular weight ester. One increasingly popular polyester (for other reasons) is the sucrose octaester used as a fat substitute in food products. After some processing, a small quantity of this ester was obtained from a bag of potato chips. A thermo gravimetric analysis (TGA) (426°F, air 50 ml/min, 9 hrs) of this yellow solid lost 30% of its mass over the nine-hour period. The Air Force basestock under the same conditions lost 90% of

its mass over the same time period. We were surprised with this result, since we expected the performance of the sucrose octaester to be comparable to the ester base stock currently in use. However, ester cleavage is still a problem, even with the higher molecular weight esters.

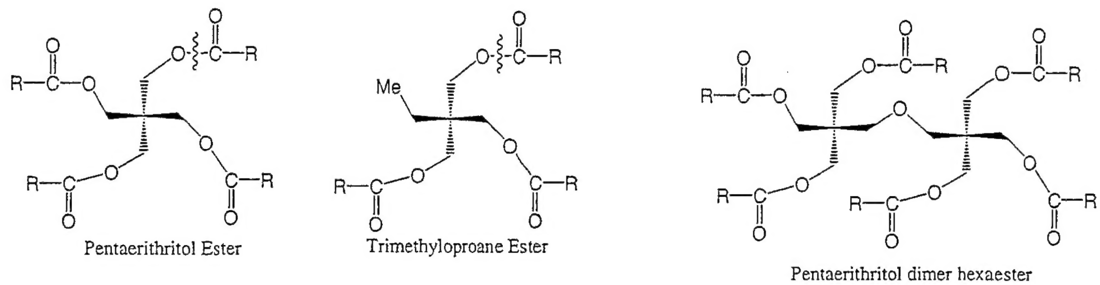

Figure 1. Turbine Engine Lubricant Esters R = hydrocarbon

POSS compounds are thermally stable, high-melting solids at temperatures > 932°F (2). With an eye towards our previous successes with increasing the use temperature of polymers by the addition of POSS (2), we focused our attention to the increasing the use temperature of lubricants using POSS. The goal of the research was to synthesize a POSS molecule that would operate (delete) between -40°F and 450°F. Prior to this time, a POSS oil had never been synthesized and we did not know if a POSS with a high molecular weight Si_8O_{12} core could be an oil.

2. EXPERIMENTAL

2.1 Materials

?

POSS materials (Hybrid Plastics) were used as received. $T_8[(CH_2CH_2)SiMe_2Octyl]_8$ was prepared by the hydrosilation of $Vinyl_8T_8$ (Figure 3) and octyldimethylsilane. $Octyl_8T_8$ was prepared by the cross metathesis of $Vinyl_8T_8$ and octene (4) with subsequent hydrogenation of the $Octenyl_8T_8$.

3. RESULTS AND DISCUSSION

We overcame the hurdle of liquefying POSS by the synthesis of POSS oil $T_8[(CH_2CH_2)SiMe_2Octyl]_8$ (Figure 2). Although this material did not have the thermal stability required, it demonstrated conclusively that a POSS oil can be synthesized.

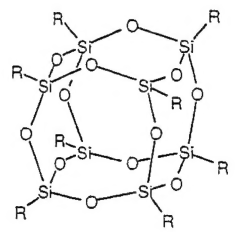

Figure 2. POSS oil $T_8(CH_2CH_2SiMe_2C_8H_{17})_8$

During the investigation into possible degradation pathways for the above POSS molecule, we discovered the molecule was decomposing at the $SiCH_2CH_2Si$ linkage. This linkage was removed by using a different pathway to make alkyl POSS compounds as shown in Figure 3. This very versatile technique in the synthesis of POSS alkyls is known as cross metathesis. Using the cross metathesis technology, a mixture of alkyl chains can be attached to the POSS molecule by adding different olefins, then hydrogenating the mixture to obtain a saturated compound. The first compound we synthesized using this method was $T_8(Octyl)_8$. A pure sample of this compound was a crystalline solid that melted at 165°F and TGA results showed that the thermal properties of this material fared quite well by losing only 27% of its mass over 9 hours (Air 420 °F). When a *single* ethyl group replaces one of the octyl groups (on average), the POSS molecule becomes a grease that melts at 113°F while retaining the thermal properties of $T_8(Octyl)_8$. The eight functional groups on the POSS cage allow the viscosity of the POSS

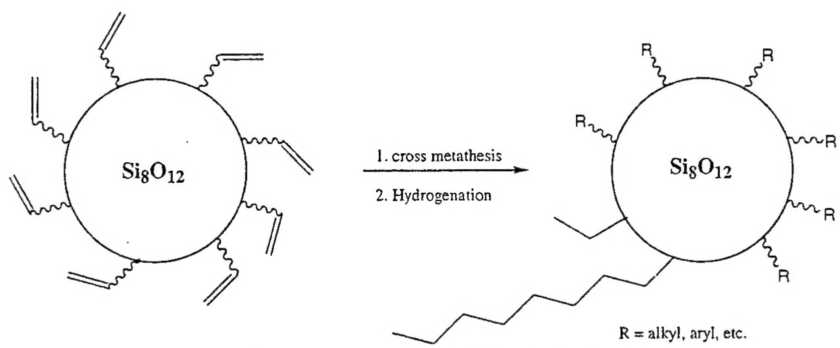

Figure 3. Cross metathesis for POSS alkyls synthesis

on the same molecule to vary, similar to mixing different oils to reach the right viscosity. When $T_8(Octyl)_{4.5}(4\text{-methylpentyl})_{3.5}$ was synthesized by cross metathesis/hydrogenation, an oil that melts at 14°F (a 99°F improvement) was obtained. This POSS oil has a viscosity of 1650 centipoises at 32°F and 1 centipoises at 392°F and the thermal properties of the earlier POSS alkyls are retained.

We are also investigating another class of POSS compounds, the cyclohexylT_2 system. The synthesis of these compounds occurs by the hydrosilation of an olefin to a cyclohexylT_2 tetrahydride (see Figure 4). Since early results looked promising, we tested the material for

viscosity. Surprisingly, the material had a viscosity of 2600 centipoises at –40°F and 28000 centipoises at –76°F. Unfortunately, the material volatilized below 400°F. We will perform more work with this material to increase the operating temperature.

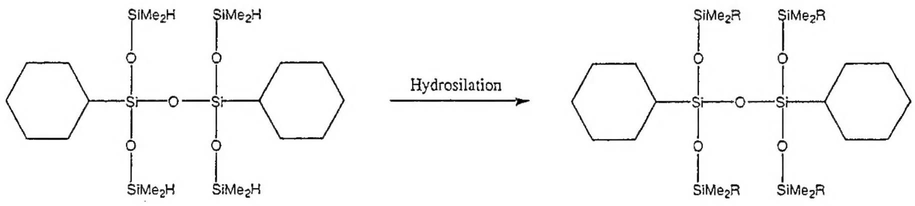

Figure 4. Hydrosilation of an olefin to cyclohexylT_2 tetrahydride

4. CONCLUSIONS

It has been shown that stable POSS oils were synthesized, characterized and tested for use as a lubricant and that they have the proper viscosity at low temperature. While the first POSS oil was not stable at elevated temperatures, the concept that a POSS cage can be an oil was shown. The second generation of POSS oil that was synthesized was shown to be stable at elevated temperature and was also an oil at low temperatures. The low temperature viscosity breakthrough came with the cyclohexylT_2 oils which had an acceptable viscosity at -40 °F. With very few alternatives for high-operating temperature oils that are pumpable at -40 °F, POSS lubricants represent a potentially large payoff for gas turbine manufacturers and users. We are still pursuing the goal of a 600°F lubricant, which may be attainable with POSS lubricants. A lubricant that is stable at 600 °F could result in the development of a new engine with a 1.5 to 1.6 times improvement in the thrust-to-weight ratio. Future work will focus on achieving this high temperature limit.

5. ACKNOWLEDGMENTS

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